

# Chemistry Revision Themes

## Part IIIc

### Themes:

#### Miscellaneous Topics

(Drugs,  
Esters, Fats & Oils,  
Motor Oil & Unsaponifiables,  
Flavouring Agents,  
Properties & Uses of Polymers,  
Biodegradability of Plastics,  
Ores, Carbon dioxide &  
Sulphur dioxide emissions,  
Radiocarbon Dating)



## CONTENT

First Year (AS) Chemistry guide: ■ First Year (A2) Chemistry guide: ■

(NB: Consult *your* examining board syllabus to establish precise requirements)

### Part IIIc:

#### Theme Seventeen: Miscellaneous Topics

201

Drugs, Nitrogen fertilizers, Esters, Fats & Soaps, Motor oil & Unsaponifiables, Properties & uses of polymers, Ores, Radiocarbon dating.

# Theme Seventeen

## Miscellaneous Topics

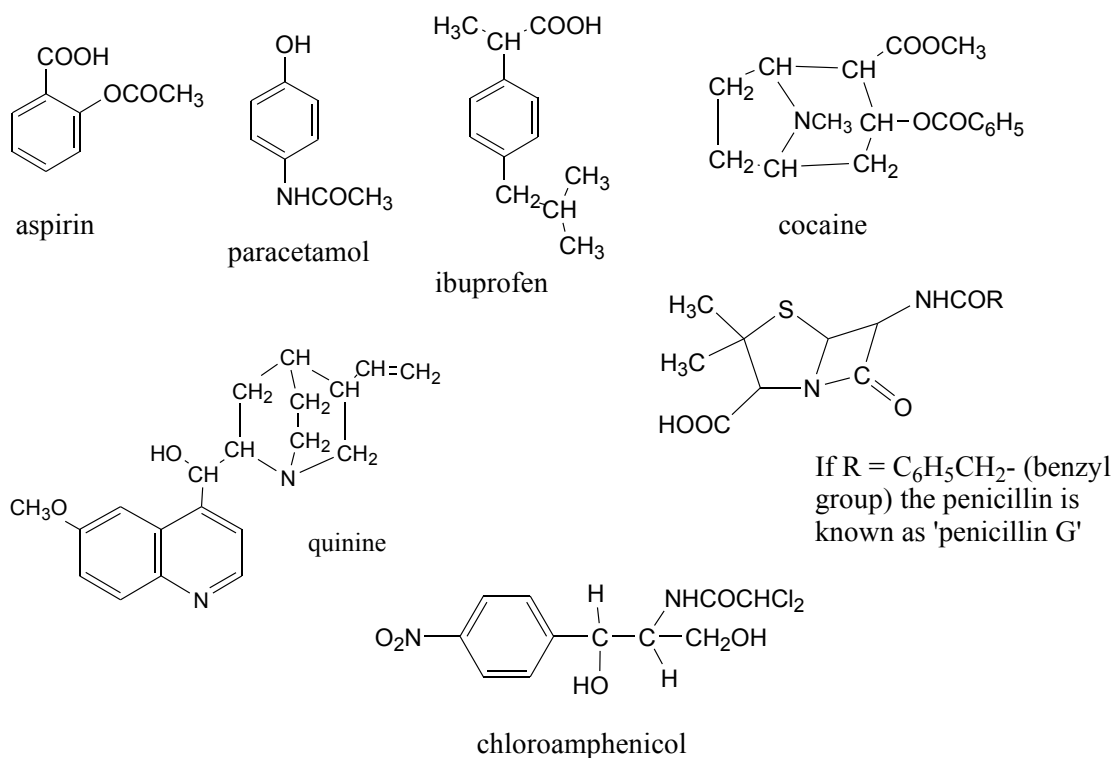
### Drugs

In the medicinal context, the term drug, refers to a variety of substances which in some way, directly or indirectly, are concerned with maintaining our good health. Most of these substances are described in the British Pharmacopoeia.

For our purpose we can classify drugs into two groups:

- (1) Those which are soothing and/or pain killing (often affecting the autonomic nervous system -the involuntary nervous system).
- (2) Those which are chemotherapeutic (control parasitic infection in man by direct chemical action with the parasite).

Included in the first group of drugs are, cocaine, morphine, codeine, aspirin, paracetamol, ibuprofen and the general anaesthetics, ether, chloroform, cyclopropane and halothane. Belonging to the second group are quinine, the sulphonamides and the antibiotics such as penicillin, streptomycin, chloromycetin and chloroamphenicol. The structures of some of these are illustrated below.



Inspection of these drug molecules shows that they have a variety of structures and functional groups. The molecules illustrated all contain polar and non-polar groupings.

The therapeutic action of these drugs depends on solubility and molecular structure. The molecule must be sufficiently soluble in body fluids and tissues to reach the site of the infection and it must have the correct shape and chemical activity to engage with and combat the infection.

Solubility is important because if a drug molecule is too soluble in water it will be excreted through the liver and kidneys before it has a chance to reach the site of the infection. Its residence time in the blood stream and body tissues will be too short for it to be active. Similarly, if it is too insoluble it will quickly pass through the gut and be excreted.

If a drug contains polar groups such as, -OH, -COOH, -COO<sup>-</sup>, NH<sub>2</sub> and -NH<sub>3</sub><sup>+</sup> its solubility in water will be enhanced whereas hydrocarbon groupings such as, -CH<sub>3</sub>, -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> and C<sub>6</sub>H<sub>5</sub>- will reduce its solubility in water. The polar groupings are referred to as hydrophilic groups (attracted to water) and the non-polar hydrocarbon groups are known as lipophilic groups (attracted to fatty tissue).

Clearly, a drug must have the optimum structural features for it to be active. It must have just the right solubility and molecular shape. Having discovered a molecule with therapeutic activity the chemist is interested in investigating the effect of small structural modifications on its activity. Does introducing a hydrophilic or lipophilic group give the molecule increased therapeutic activity? Furthermore, the chemist is interested in discovering other molecules with similar structural features to see if they to have therapeutic activity.

Aspirin is a case in point. This compound was first synthesised in 1853 by Charles von Gerhardt and first used as a drug to treat fever and pain (antipyretic and analgesic) in 1898. It replaced its close relative, salicylic acid (2-hydroxybenzenecarboxylic acid) which was being administered in large doses for the control of rheumatism. Aspirin has the advantage of being much less aggressive towards the lining of the stomach and being more lipophilic is a more efficient antipyretic and analgesic. Aspirin is also prepared as the sodium salt so that it can be dispersed in water for ease of swallowing. Paracetamol and ibuprofen are more recent alternatives to aspirin. The three drugs have some similar structural features.

Chloroamphenicol was discovered in 1947 by John Ehrlich and Quentin Bartz. It was the first broad-spectrum antibiotic being active against a variety of diseases including typhus. It suffers from the disadvantage of causing aplastic anaemia in about 1 in 50 000. However, it is still used in combination with other drugs and can be used safely for treating eye and ear infections. The molecular structure has both hydrophilic and lipophilic groupings. Replacing the hydroxyl group by the ester-salt group (sodium succinate group),  $-\text{OOCCH}_2\text{CH}_2\text{COO}-\text{Na}^+$ , makes the molecule more hydrophilic and enables the drug to be intravenously injected (rather than being taken by mouth).

The antibacterial action of penicillin was discovered by Sir Alexander Fleming in 1928. However, it was not until 1940 that the potency of penicillin against streptococci in mice was established. Hospital patients were first successfully treated in 1941. The structure of penicillin was established at Oxford in 1945 by Dorothy Hodgkin using X-ray crystallography.

Since these times numerous penicillin derivatives have been synthesised with a view to improving the characteristics of the original penicillin-G. This penicillin is very soluble in water, it is relatively unstable in the acid conditions of the stomach, it has a narrow spectrum of activity against diseases and it has low resistance to degradation by certain microorganisms.

Penicilli-V, in which the group R is  $-\text{CH}_2\text{OC}_6\text{H}_5$ , has good stability to acid conditions and is therefore a useful oral antibiotic. Ampicillin, in which  $\text{R} = -\text{CH}(\text{NH}_2)\text{C}_6\text{H}_5$ , is also good in acid conditions and has a broader spectrum of activity than penicillin-G.

## Nitrogen Fertilizers

Plants take up nitrogen through their roots in the form of dissolved nitrate ( $\text{NO}_3^-$ ).

They use this nitrogen to synthesise protein and nucleic acids (DNA/RNA).

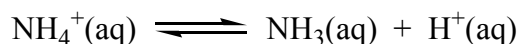
The soil also contains bacteria which are capable of converting ammonium ion ( $\text{NH}_4^+$ ) and other nitrogen containing compounds into nitrate ion. The significance of this is that farmers can apply a variety of nitrogen containing substances and compounds to provide the nitrate ion essential to plants.

In practice, farmers apply natural fertilizers such as potassium nitrate, farmyard manure and slurry and synthetic fertilizers such as ammonium nitrate, ammonium sulphate and urea to improve the natural nitrate composition of soils.

### Advantages and Disadvantages of Synthetic Nitrogen Fertilizers

The ammonium salts, ammonium nitrate and ammonium sulphate are readily available from reactions of ammonia (made by the Haber process) with nitric acid (from the Ostwald process) and sulphuric acid (from the Contact process).

Both salts are very soluble in water providing slightly acidic solutions due to dissociation of the ammonium ion. ie,



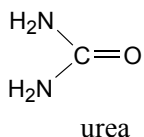
Ammonium nitrate has a potential to explode; when heated it readily decomposes into nitrogen(I) oxide and water. Care must be exercised in the manufacture, packaging, transport and use of the salt.

The ammonium salts are readily introduced into the soil by spreading on the surface and allowing the rain to wash them in. However, solubility can be a mixed blessing because excessive rain may wash the salts out of the soil and into ditches, streams and rivers before they have a chance to be taken up by the crops. Apart from this being an inefficient use of the fertilizer it can be detrimental to water courses. The salts can cause excessive growth of algae which can clog up the waterway and reduce the oxygen content of the water. High concentrations of these salt are directly or indirectly harmful to aquatic creatures.

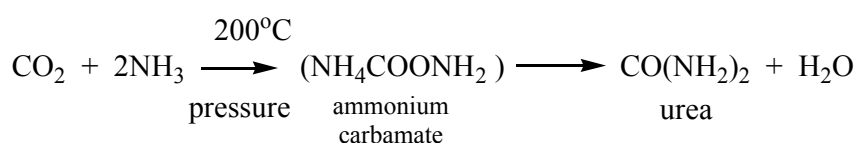


Careless and excessive application of ammonium salts to fields can cause overgrowth of foliage at the expense of the flower and fruit development. There is also the possibility of burning and shrivelling of young plants if they remain in direct contact with the fertilizer for some period of time. Another possibility is plant damage as a result of reverse osmosis. This can happen when the concentration of ions in aqueous solutions in the soil, exceeds the concentration of solutes in the plant fluids. Then, instead of water being taken up by the plant from the soil, it loses water to the soil.

The organic compound, urea, provides another important source of nitrogen for plants. It is the chief nitrogen containing compound excreted by mammals and it can be applied to the land in the form of farmyard manure and slurry.



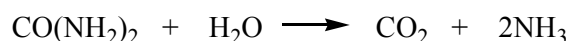
Urea is also synthesised and applied to the soil. It is made by reacting carbon dioxide with ammonia at about 200°C and at high pressure. Ammonium carbamate is formed which then readily dehydrates to urea.



Urea is a white crystalline solid containing 46% nitrogen (this compares with 35% in ammonium nitrate). It is freely soluble in water and its solution is neutral (unlike ammonium salt solutions which are acidic). Like ammonium salts it may be washed away by heavy rain.

It has the advantage of releasing its nitrogen slowly by hydrolysis.

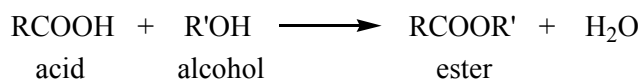
ie,



## Esters, Fats and Soap.

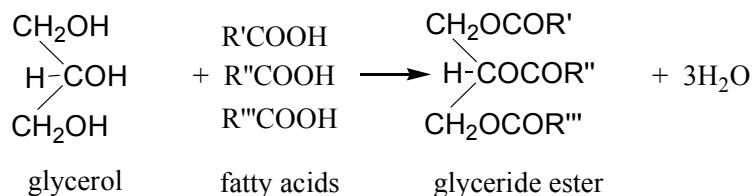
Esters are compounds formed from carboxylic acids and alcohols.

ie,



Vegetable oils and animal fats contain a high proportion of esters made from the triol, propane-1,2,3-triol (glycerol), and a variety of carboxylic acids (known as fatty acids).

Ie,



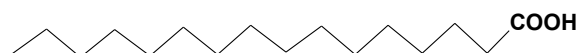
The fatty acids have relative molecular masses in excess of 220 and commonly contain 14 to 20 carbon atoms per molecule.

This means that the resulting esters have very high relative molecular masses and are high boiling liquids or low melting solids.

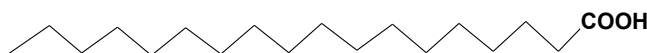
Palmitic, stearic and oleic acids occur most frequently in triglycerides.

Palmitic acid (16 carbon atoms) and stearic acid (18 carbon atoms) are saturated acids.

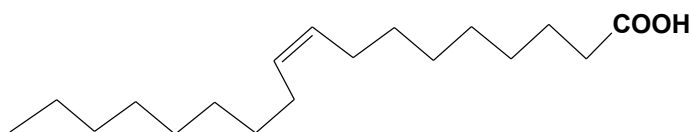
Oleic acid (18 carbon atoms) is an unsaturated fatty acid; it contains one carbon-carbon double bond.



**palmitic acid**



**stearic acid**



**cis oleic acid**

Saturated fatty acids have higher melting points than unsaturated fatty acids.

Also, unsaturated fatty acids with a cis conformation have lower melting points than those with the trans conformation.

eg

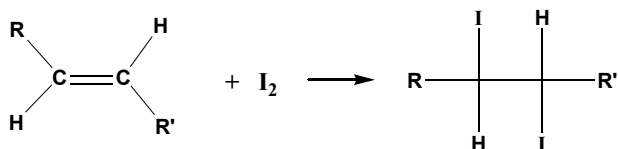
stearic acid (18 C) mp 70°C

oleic acid (18 C, 1 cis double bond) mp 11°C

elaidic acid (18 C, 1 trans double bond) mp 44°C

The main reason for this is that saturated and trans unsaturated fatty acid molecules are able to pack together effectively and establish strong van der Waal forces. Because of distortion at the double bond, the cis unsaturated molecules are unable to pack together effectively.

All oils and fats contain a proportion of unsaturated fatty acid in the triglycerides. This proportion is often measured as the **iodine value** (or *iodine number*). Iodine combines readily with unsaturated compounds adding across the carbon-carbon double bond in a quantitative manner.



The iodine value is usually expressed as the grams of iodine which combines with 100g of the oil or fat. Olive oil, for instance, has an iodine value in the range 80 - 90. Butter has an iodine value in the range 26 - 38. Olive oil, therefore, contains a higher proportion of unsaturated acids than butter.

Large quantities of purified **vegetable oils** are hardened and converted to margarine.



This is achieved by reacting the oil with hydrogen, using nickel as a catalyst.

The process is operated at about 170°C and 4 atmospheres pressure. Partial hydrogenation of the oil occurs reducing the unsaturation to a lower level. This results in the formation of a semi-solid fat. Further hydrogenation produces a fat which is too hard.

Hydrogenation also produces a fat which is more stable than the original oil. The remaining unsaturated fatty acids are mostly converted to the trans isomers during the hydrogenation which also contributes to the hardening process. Research has shown that excessive amounts of saturated fats may cause furring of the arteries (ie, build up of cholesterol) and heart disease.

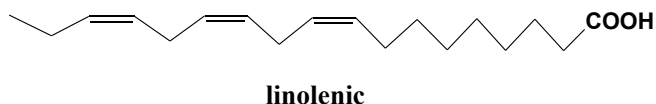
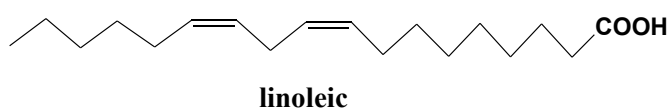
Butter contains a high proportion of saturated fats.



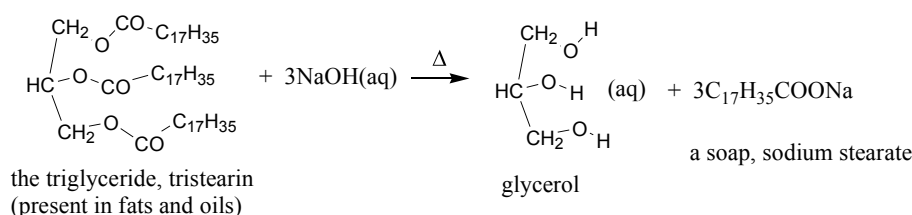
A certain amount of unsaturated fats, in our diet, is beneficial. The unsaturated fatty acids, linoleic (18 C and 2 non-conjugated double bonds) and linolenic (18 C and 3 non-conjugated double bonds) are particularly valuable.

Fats and oils containing unsaturated fatty acids with two or more double bonds are referred to as being **polyunsaturated**.

To provide these essential unsaturated fatty acids, margarine is often blended with fats and oils rich in polyunsaturates (eg, sunflower oil, peanut oil and corn oil).



Soaps are the sodium or potassium salts of fatty acids. They are prepared by refluxing animal and vegetable oils with sodium or potassium hydroxide solution. During this process, the triglycerides are hydrolysed to glycerol and fatty acids. The fatty acids are present in the reaction mixture as sodium or potassium salts and these may be separated by salting-out with sodium chloride. The molten fatty acid salts float on the surface of the reaction mixture and can be isolated by running off the lower aqueous layer. The molten soap is dyed and perfumed and then cooled and when solid, cut into bars. Glycerol is obtained from the aqueous phase by distillation. The hydrolysis of the triglycerides is often referred to as saponification since it provides soaps.

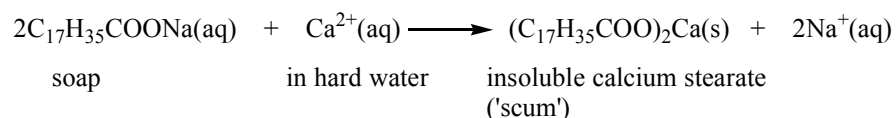


Soaps containing potassium are softer and more soluble than those containing sodium.

Calcium hydrogencarbonate, in domestic water, causes the water to be temporary hard. This type of hardness can be removed by boiling the water which converts soluble calcium hydrogencarbonate into insoluble calcium carbonate. Calcium sulphate causes water to be permanently hard; it cannot be removed by boiling.

Soaps soften hard water by forming insoluble salts with the calcium ion which is responsible for the hardness. The insoluble calcium salt appears in the water as a grey solid, known as scum.

eg,

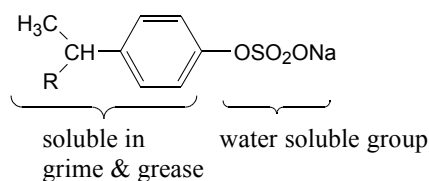


Once the hardness (calcium ion) has been removed, excess soap will form a lather when agitated in the soft water. The soap will also remove particles of grease from clothes, during washing, by helping to disperse the grease particles in the water.

The disadvantage of using soap to wash clothes is that it forms an insoluble calcium salt which forms scum on the surface of the water and on the fibres of the clothes. **Detergents** form calcium salts which are much more soluble in water and consequently form little or no scum.

The most widely used detergents have a sulphonate group attached to a large hydrocarbon group.

eg,



where R = alkyl group with 8-12 carbon atoms



### Motor Oil and Unsaponifiabiles.

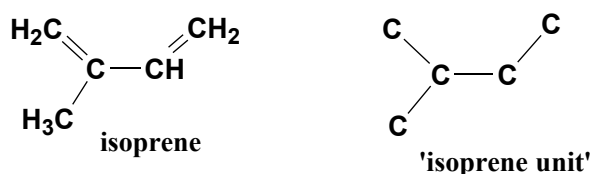
Motor oils are obtained from crude oil. Deposits of crude oil occur throughout the World. Large deposits are found in countries of the Middle East, Russia, and the USA and in the North Sea.

Wells are drilled to the oil deposits and natural gas pressures force the oil to the surface. Crude oil is then fractionally distilled to separate it into various boiling fractions. The high boiling, heavy oil, fraction provides lubricating oil used in petrol and deisel engines; it contains mostly saturated hydrocarbons having more than 25 carbon atoms per molecule.

Unsaponifiabiles are substances found in vegetable oils which cannot be broken down by treating with dilute alkali. They include, simple hydrocarbons, terpenic hydrocarbons, alcohols, aldehydes and ketones, and sterols; they are not esters. These compounds account for only about 2% of the common vegetable oils but they are the main constituents of the so called **essential oils** of some plants. The essential oils are contained in the stems, fruits and seeds of some plants and have characteristically strong odours. They may be isolated by **steam distillation** of the chopped and macerated plant material.

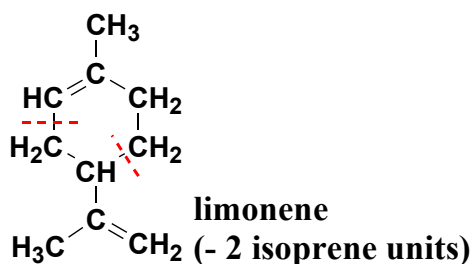
**Terpenes** are the major constituents of **essential oils**. Their structures are composed of several isoprene units, where an isoprene unit consists of a branched five carbon atom chain.

ie,



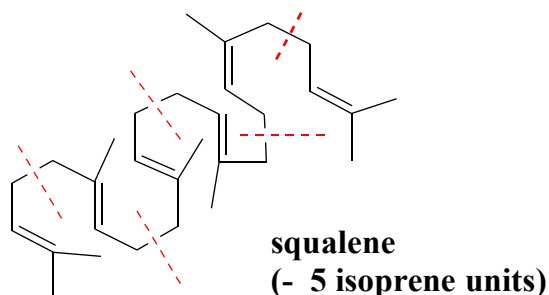
The essential oil from orange peel consists mostly of limonene.

Ie,



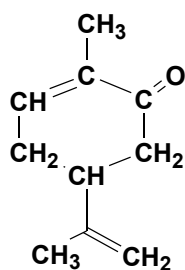
Squalene is a more complex terpene found in some essential oils and also in shark liver oil. It is an intermediate in the biosynthesis of steroids

Ie,

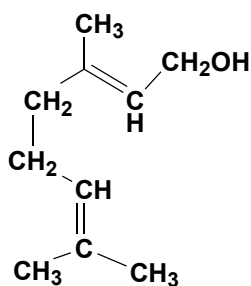


A variety of terpenes contain oxygen, present in carbonyl and hydroxyl groups.

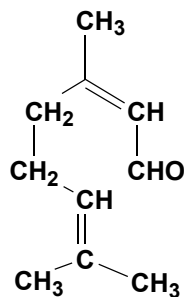
eg,



**carvone**  
(in oil of caraway)



**geraniol**  
(in rose oil)

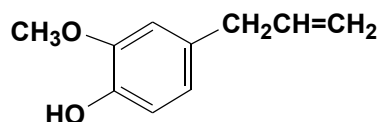


**citral**  
(in oil of lemongrass)

## Flavouring Agents

For thousands of years foods have been treated with salt and herbs to give it a pleasant smell and taste. Pepper, cloves, ginger, vanilla, peppermint, orange and lemon are important natural flavouring agents. All of these contain quantities of essential oils which account for their characteristic smell and taste.

eg, clove oil is a complex mixture of chemicals, however, the main constituent is *eugenol* (85%)



The main chemical constituents of essential oils are commercially available.

They can be blended together and used to provide a variety of food flavours.

Many fruit flavours are due to the presence of esters. These have been isolated, identified and synthesised to provide artificial fruit flavours.

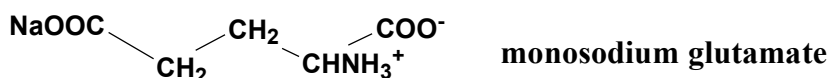
eg,  
ethyl methanoate used in rum, peach and raspberry flavours.

*ethyl ethanoate* used in apple, pear and strawberry flavours.

*pentyl butanoate* used in banana and pineapple flavours.

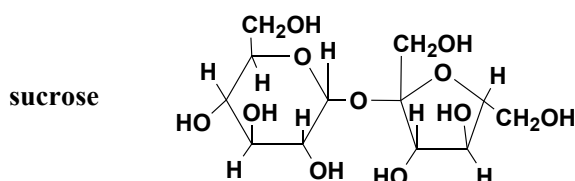
Some chemicals have the ability to modify flavours when added to foods.

**Monosodium glutamate** is the best known example and is used to enhance the flavour of meat dishes.



A tropical berry is known ('*miracle berry*') which contains the glycoprotein, *miraculin*, which is able to make sour-tasting foods taste sweet.

The disaccharide, sucrose, is the main natural food sweetener. However, a large variety of synthetic sweeteners are commercially available, eg, saccharin, aspartame and acesulfame-K.



## Properties and uses of polymers.

### Addition Polymers.

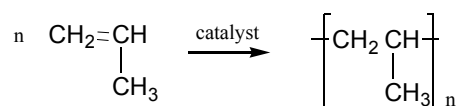
**Polyethene:** Low density polyethene is made by heating ethene at 200°C and 1500 atmospheres in the presence of a trace of oxygen which acts as catalyst.



High density polyethene is made by polymerising ethene in the presence of triethylaluminium and titanium(IV) chloride (Ziegler-Natta catalyst) at about 70°C.

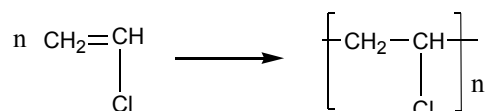
Low density polyethene has the lower softening temperature (about 120°C) and is used for making plastic film and bags. The high density polymer is used to make bowls and buckets and piping.

**Polypropene:** Propene is polymerised using the Ziegler-Natta catalyst.



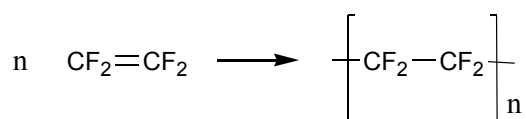
Polypropene is stiffer and harder than polyethene it is used to make fibre for ropes and carpet, car components and household goods.

**Polychloroethene:** Like ethene, chloroethene (vinyl chloride) is readily polymerised forming polychloroethene (polyvinyl chloride, PVC).

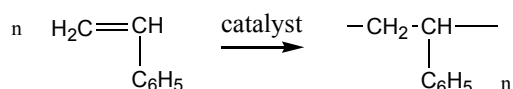


This is a rigid plastic which can be made flexible by adding plasticizers (such as alkyl phthalates). The flexible plastic is used to make squeeze bottles, imitation leather upholstery, guttering and gas and water pipes.

**Polytetrafluoroethene:** Polytetrafluoroethene (PTFE) has a relatively high softening temperature (about 327°C). As a result, it is resistant to heat. It is also resistant to the action of chemicals. It has a low coefficient of friction and is used to make joints and bearings. It is used to make non-stick surfaces for saucepans and frying pans.

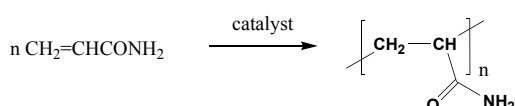


**Polyphenylethene (Polystyrene):** Phenylethene (styrene) is readily polymerised to give a hard, brittle, plastic.



It can be made softer by blending with a small amount of polybutadiene or styrene-butadiene rubber. The polymer finds wide application in packaging and building trades where it is used as a foam (expanded polystyrene foam). Blocks and sheets of this material have excellent heat insulation properties. Its disadvantage is that it is highly flammable although this can be reduced by adding non-flammable material during the expansion process. The plastic is also used to make, clear sheet, food containers, toys and electrical goods. Another application is as a car body filler. Styrene, mixed with an inert filler, is treated with a peroxide catalyst when it polymerises and sets to a hard mass which is then smoothed, sanded and painted to blend with the original body work.

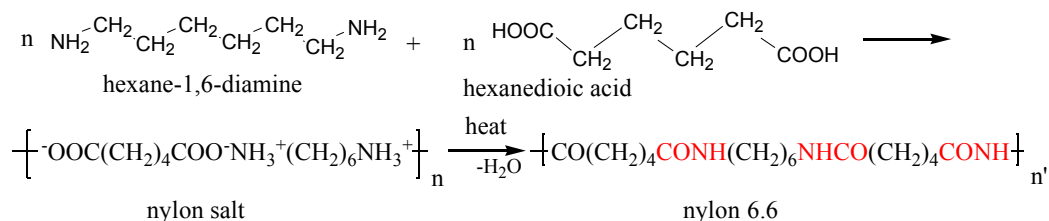
**Polyacrylamide (poly(propenamide)):** Made from acrylamide (prop-2-enamide). It has the ability to absorb water forming gels. It is used as, a flocculent in the process of purifying water, an electrophoresis gel, a binder in paper manufacture, a component of contact lenses and a constituent of some toys (which expand when treated with water!).



Its affinity for water is due largely to its ability to form H-bonds employing the amide groups.

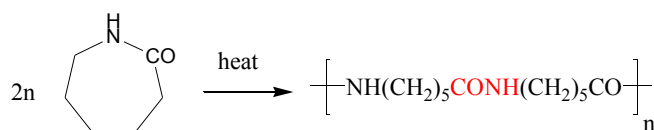
## Condensation Polymers.

**Nylon:** This is a polyamide and it is an example of a condensation polymer because water is lost during the polymerisation process. Nylon 6.6 is made by heating together, hexane-1,6-diamine and hexanedioic acid. Both of these reactants contain six carbon atoms per molecule and combine to form a salt which on heating to about 250°C loses water to form nylon.



(n and n' are large numbers of molecules and segments of molecules)

Another form of nylon is nylon 6 which is made from caprolactam.



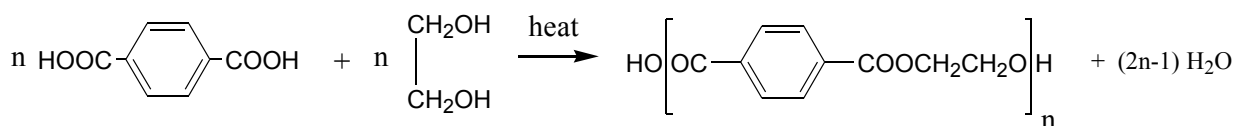
Nylons are used to make synthetic fibres for clothes and ropes. Since they are tough and have a low coefficient of friction they are also used to make bearings, wheels and cogs for light machinery.

Some condensation polymerisations involve the loss of small molecules other than water. In some cases ammonia, hydrogen chloride or methanol are lost.

**Terylene:** This is a polyester. It is made by reacting benzene-1,4-dicarboxylic acid (terephthalic acid) with ethane-1,2-diol.

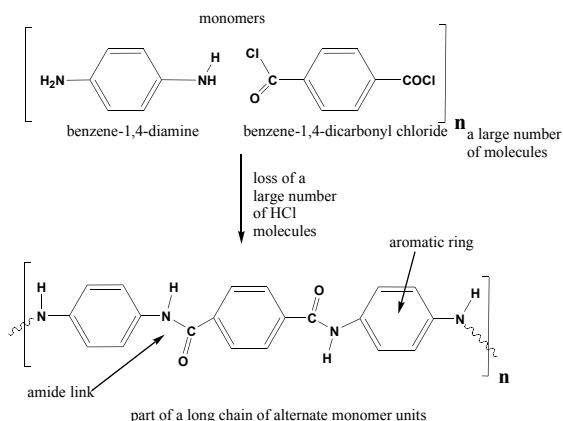
In practice, the dimethyl ester of terephthalic acid is used and methanol is the small molecule eliminated.

Terylene is used to make fibre for clothes. Terylene fibre is usually mixed with cotton fibre to improve wear and appearance.



**Kevlar:** Like Nylon this is a polyamide, however, unlike Nylon, it is an *aromatic* polyamide. It was invented by the American chemist, S. Kwolek working for the chemical company, Dupont, in 1965. It is renowned for its strength and ability to resist strong impact and, as a result, is used for the manufacture of body armour, crash helmets, protective gloves, boat hulls and sails and even boot laces!

The strength of this plastic is due to the very strong intermolecular forces acting between aligned polymer chains, particularly H-bonding involving the NH & CO groupings.

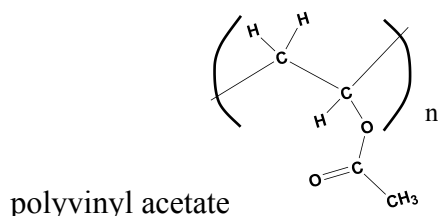




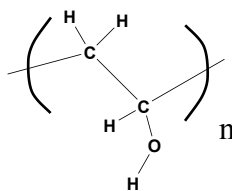
## Biodegradability of Plastics.

Synthetic polymers such as polyethene, polyvinyl chloride and polystyrene are highly resistant to chemical and bacterial action. As a result they survive for long periods before breaking down and becoming assimilated into the soil (eg, 500 years or more!). Sunlight, which provides ultra-violet light, speeds up the degradation of plastics by breaking bonds within the polymer chains allowing oxidation. This causes the plastic to become brittle and powdery. In landfill sites where the plastic is not exposed to sunlight it is very gradually broken down by the action of bacteria. However, bacterial action is most effective if the polymer chain is partially oxidised, ie, if it contains some polar oxygen containing groups, eg, polyvinyl alcohol and polyvinyl acetate. Incorporating catalytic transition metal compounds into the plastic also helps with degradation of the plastic.

Polyvinyl acetate and polyvinyl alcohol are examples of more environmentally friendly polymers.



polyvinyl acetate

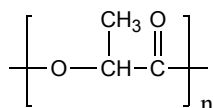


polyvinyl alcohol

Polymerisation of vinyl acetate gives polyvinyl acetate and hydrolysis of this provides polyvinyl alcohol (PVA). By controlling the extent of hydrolysis polymers can be made which have varying degrees of solubility in water. A mixture of polyvinyl alcohol and polyvinyl acetate in the ratio 9:1 is freely soluble in water. Polymer mixtures such as these find a variety of uses relating to their water solubility. Some laundry bags and detergent pouches, for example, are made from PVA. Under the conditions of a 40-50°C wash these bags break up and dissolve, spilling their contents into the washing machine.

PVA is also used in a variety of glues or adhesives. It is also incorporated into concrete to improve its strength and workability.

A number of new biodegradable plastics have been developed and are being used to make various types of plastic containers for foods and dry goods. Polylactic acid (PLA) is one example. The lactic acid is produced by bacterial fermentation of carbohydrates (from corn crops) and then chemically polymerised to give a high melting crystalline plastic.



The main drawback at present is the price compared with conventional plastics. PLA costs about £3 per kg whereas polystyrene cost about £0.60 per kg. However, the prices of these new polymers is coming down all the time. Some years ago PLA cost £38 per kg!

# Ores

Ore, is that material in the earth's crust (the *lithosphere*) from which metals can be profitably be extracted. Most of the lithosphere is comprised of the non metals oxygen (46.5%) and silicon (27.5%); the **total** metal content is about 25%.

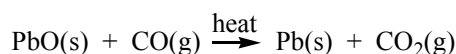
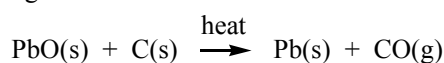
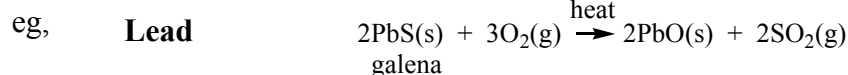
Most of the metals occur in the combined state very few are found in the *native* state (ie, as the uncombined metal). Due to their resistance to reaction with water, air and acidic gases the metals copper, silver, gold, palladium and platinum have all been found in the native state.

The most abundant metal in the earth's crust is aluminium. One would expect, therefore, the metal to be inexpensive and readily available. However, most aluminium occurs, in the earth's crust, as aluminosilicates (in clay soil) and at the present time it is not commercially viable to extract it from this material. The main commercial ore is bauxite and this is much less widely distributed; it is a limited global resource.

## The main ores of some of the most abundant metals in the earth's crust:

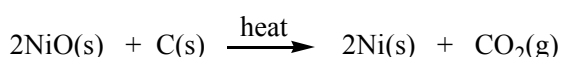
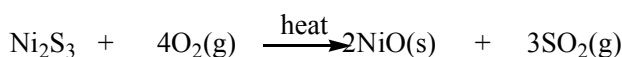
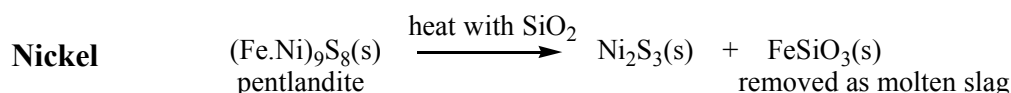
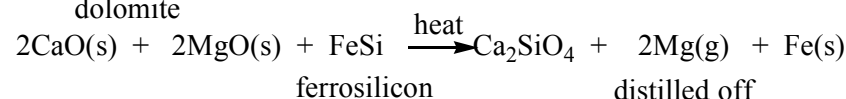
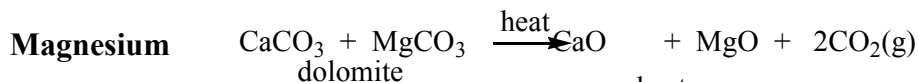
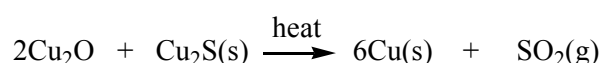
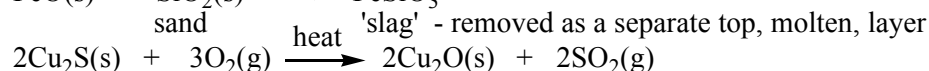
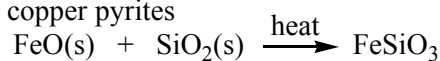
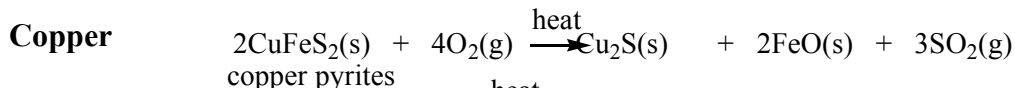
Metal	Main Ores
aluminium	bauxite (contains $\text{Al}_2\text{O}_3$ )
iron	haematite ( $\text{Fe}_2\text{O}_3$ ) & magnetite ( $\text{Fe}_3\text{O}_4$ )
calcium	limestone ( $\text{CaCO}_3$ ), dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ )
magnesium	dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), magnesite ( $\text{MgCO}_3$ )
sodium	sodium chloride ( $\text{NaCl}$ ), trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ )
potassium	sylvine ( $\text{KCl}$ ), carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ )
titanium	rutile ( $\text{TiO}_2$ ), ilmenite ( $\text{FeTiO}_3$ )
manganese	pyrolusite ( $\text{MnO}_2$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ )
barium	barytes ( $\text{BaSO}_4$ ), witherite ( $\text{BaCO}_3$ )
strontium	strontianite ( $\text{SrCO}_3$ ), celestine ( $\text{SrSO}_4$ )
zirconium	zircon ( $\text{ZrSiO}_4$ ), baddeleyite ( $\text{ZrO}_2$ )
vanadium	vanadinite ( $\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{VO}_4)_2$ ), carnotite ( $\text{K}_2\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$ )
chromium	chromite ( $\text{FeCr}_2\text{O}_4$ )
nickel	pentlandite ( $\text{FeNi}_9\text{S}_8$ )
rubidium	rubidite ( $\text{RbK})(\text{AlSi}_3\text{O}_8)$ , also occurs in K bearing ores; carnallite and lepidolite
zinc	zinc blende ( $\text{ZnS}$ ), zinc spar ( $\text{ZnCO}_3$ )
copper	copper pyrites ( $\text{CuFeS}_2$ ), malachite ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ )
cerium	monazite sand (mixed lanthanide phosphates) Ce makes up about 50% of the metal content
neodymium	monazite sand (mixed lanthanide phosphates) Nd makes up about 18% of the metal content
lanthanum	monazite sand (mixed lanthanide phosphates) La makes up about 20% of the metal content
praseodymium	monazite sand (mixed lanthanide phosphates) Pr makes up about 5% of the metal content
cobalt	cobaltite ( $\text{CoAsS}$ ), smaltite ( $\text{CoAs}_2$ )
scandium	thortveitite ( $\text{Sc}_2(\text{Si}_2\text{O}_7)$ )
niobium	pyrochlore ( $(\text{CaNa})_2\text{Nb}_2\text{O}_6(\text{OH},\text{F})$ ), columbite ( $(\text{Fe},\text{Mn})(\text{Nb},\text{Ta})_2\text{O}_6$ )
lithium	spodumene ( $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ ), amblygonite ( $2\text{LiF} \cdot \text{Al}_2\text{O}_3 \cdot \text{P}_2\text{O}_5$ )
lead	galena ( $\text{PbS}$ )
uranium	pitchblende ( $\text{U}_3\text{O}_8$ ), carnotite ( $\text{K}_2\text{O} \cdot 2\text{UO}_3 \cdot \text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ )
tin	cassiterite (tinstone) ( $\text{SnO}_2$ )
tungsten	wolframite ( $\text{FeWO}_4 \cdot \text{MnWO}_4$ ), scheelite $\text{CaWO}_4$ )
silver	native metal ( $\text{Ag}$ ), argentite ( $\text{Ag}_2\text{S}$ ), desilverisation of lead
mercury	cinnabar ( $\text{HgS}$ )
platinum	sperrylite ( $\text{PtAs}_2$ ), cooperite ( $\text{PtS}$ ), Pt is also obtained during the isolation of nickel and copper
gold	Occurs as the metal in quartz rock

This table shows that oxides, carbonates, sulphides and arsenides are important constituents of metal ores. By heating in air many metal carbonates, sulphides and arsenides can be converted to oxides. The oxides can then be reduced to the metal by heating with carbon, carbon monoxide or hydrogen. Alternatively, particularly in the case of the reactive metals such as those in groups I and II, the oxide can be converted to chloride and this reduced electrolytically. In the case of aluminium, the fused oxide is reduced directly by electrolysis.

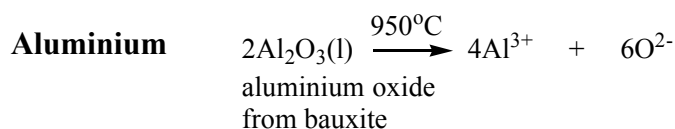
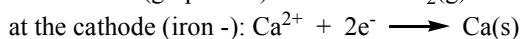
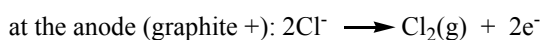
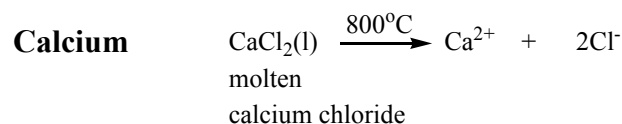
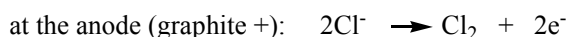
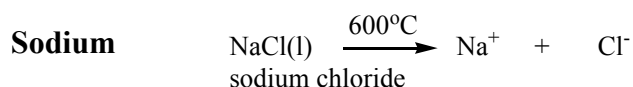


C & CO are acting as reducing agents

Similarly with zinc blende (ZnS)



## Electrolytic Processes:



## Reduction of metal oxides.

The metal oxides are often obtained by heating the sulphide ores in air. The sulphur burns off as sulphur dioxide. The sulphides cannot be reduced directly to metal, by heating with carbon or hydrogen, because the reaction products, carbon disulphide and hydrogen sulphide, are relatively unstable and their formation reactions are of low exothermicity compared with the metal sulphides themselves.

Metal oxides are generally very stable compounds. In most cases, for example, they cannot be decomposed into their elements by heating in a crucible using a hot bunsen flame. However, theoretically it should be possible to decompose any metal oxide to metal and oxygen providing the temperature is sufficiently high. The problem is that most of these decomposition temperatures are *so* high that the process is uneconomic on a commercial scale. In the case of aluminium oxide, for instance, a temperature well in excess of 3000°C is required for decomposition. Even copper oxide requires a temperature of about 1800°C (ie, about twice the temperature of a hot bunsen flame) before it will decompose into its elements. Only mercury, silver and gold oxides can be decomposed at moderate temperatures (ie, below about 500°C).

The process of decomposing metal oxides is made much easier by heating with **carbon**. Carbon will combine with oxygen forming stable carbon monoxide and the higher the temperature the more readily this occurs. This means that, providing the temperature is high enough, carbon can reduce most metal oxides to the metal as it takes up oxygen and is converted into carbon monoxide. Once again the operating temperature may limit the commercial viability of this reduction. Magnesium oxide, for instance, can be reduced with carbon but an excessive temperature, in the order of 2000°C, is required which makes the process uneconomic on a large scale! Even so, the oxides of copper, lead, nickel, iron, zinc, chromium and manganese can be reduced with carbon at temperatures below 1500°C. Carbon monoxide itself will reduce some metal oxides (eg, copper(II) oxide, lead(II) oxide and iron(II) oxide) to the metal.

**Hydrogen** can be used to reduce the oxides of copper, zinc, nickel, lead, iron and tungsten. The operating temperatures need to be fairly high (approaching 1000°C) and great care has to be exercised to ensure conditions do not allow the gas to form explosive mixtures with oxygen. On a small scale the reducing properties of hydrogen gas can be demonstrated by heating copper(II) oxide in a stream of hydrogen. The oxide can be contained in a borosilicate boiling tube which has a small hole blown in the sealed end to allow excess hydrogen to burn off. The oxide changes colour from black to salmon pink as the reduction takes place to give metallic copper.

Relatively pure samples of the metals calcium, barium, strontium, chromium, manganese and iron can be obtained from their oxides by reduction with powdered **aluminium**. The reduction is known as the **aluminothermic process** (developed by *Hans Goldschmidt* 1861-1923). The reactions usually occur very quickly and produce great heat generating temperatures in the region of 3000°C. The success of the reactions depends on the ferocious affinity of aluminium for oxygen to form the very stable aluminium oxide. The procedure adopted varies according to which metal is being extracted and for what purpose. In the case of calcium the process involves thorough mixing of aluminium powder with powdered calcium oxide and heating the mixture in steel retorts to about 1200°C. The calcium distils off under vacuum. Pure iron, for welding purposes, can be produced by heating powdered iron(III) oxide with powdered aluminium and a little barium peroxide. The mixture is ignited electrically and the molten iron run from the bottom of the steel reaction vessel into the weld. The aluminothermic process (also known as the thermite reaction) is sometimes demonstrated in the laboratory (on a small scale with adequate safety precautions!); in this case the thermite mixture is ignited with burning magnesium ribbon.

In modern times the availability of metal ores has declined as existing deposits become exhausted. New sources of the ores have to be found and new processing methods adopted for working deposits which at one time were considered uneconomic. It is now worthwhile collecting waste metal objects to recycle the metals. Copper is a good example. Old electric power cables and hot water pipes and tanks are collected and melted down to provide copper for industrial use. Low grade copper sulphide ores are sometimes crushed and piled in heaps and then sprayed with water (*hydrometallurgy*). The sulphide is oxidised to sulphate and this collected from the base of the heaps as dilute copper sulphate solution. This can be concentrated and then electrolysed to provide metallic copper. Alternatively, scrap iron can be added which displaces metallic copper from solution.

Aluminium is another good example. It is now common practice to collect old pots and pans and drinks cans to reclaim the relatively scarce and expensive metal.

## Carbon dioxide and sulphur dioxide emissions.

It may be observed that a number of the metal extraction processes produce the acidic gases carbon dioxide and sulphur dioxide. Both of these are pollutants if allowed to escape into the atmosphere.

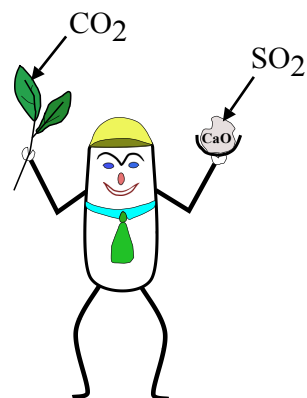
Carbon dioxide is referred to as a *greenhouse gas* because it absorbs infra red radiation and prevents heat escaping from the earth's surface.

Under normal circumstances this is desirable because otherwise the surface of the earth would be too cold. Normal concentrations of atmospheric gases help maintain an average surface temperature of about 15°C. However, excessive amounts of greenhouse gases, like carbon dioxide, can trap too much heat resulting in the surface temperature rising above this average value. This effect is known as *global warming*. One result of global warming is the melting of ice caps and the consequential rise in sea level with the possibility of flooding.

Under normal conditions the concentration of carbon dioxide in the atmosphere is controlled by terrestrial vegetation (eg, trees) and marine plants (eg, phytoplankton) which take up carbon dioxide in photosynthesis. Destroying these plants will upset the delicate balances of nature. It is important therefore to control the logging industries which deplete the rain forests and improve the design of industrial processes so that less carbon dioxide is allowed to escape into the atmosphere.

Sulphur dioxide dissolves in water forming sulphuric(IV) acid (*sulphurous acid*). When present in the atmosphere it will dissolve in rain water making it acidic (giving *acid rain*). In the upper atmosphere the dioxide is oxidised to sulphur trioxide which is also soluble in water forming the strong acid sulphuric(VI) acid. Over a period of time acid rain will lower the pH of soil and kill trees and other plants. It will get into the rivers and lakes and kill the fish and other creatures that live in these environments. A consequence of destroying vegetation is to increase the concentration of atmospheric carbon dioxide and global warming!

Responsible industries can reduce sulphur dioxide emissions by absorbing the gas on lime (CaO) or in alkaline solutions rather than allowing it to escape directly into the atmosphere. It is also possible to collect the gas and convert it into sulphuric(VI) acid which can then be used commercially.



## Radiocarbon Dating

Often referred to as ‘carbon dating’ it is an experimental procedure for discovering the age of relics containing organic material. Although not 100% accurate it has proved valuable for dating numerous archeological and geological specimens.

In 1940 the Canadian-American biochemist, Martin Karmen, discovered the radioactive isotope carbon-14 (beta emitter) occurring in biological material. It soon became apparent the C-14 occurs in biological material as a result of the fixing of carbon dioxide in the process of photosynthesis. Over the next few years it was shown that atmospheric carbon dioxide contains a small proportion of radioactive  $^{14}\text{CO}_2$  which is formed, mostly above 30 000 feet, by the action of cosmic rays on nitrogen. Cosmic rays can transform nitrogen atoms into C-14 atoms and these combine with oxygen forming  $^{14}\text{CO}_2$ . Through photosynthesis plants take up this  $^{14}\text{CO}_2$  along with ordinary carbon dioxide ( $^{12}\text{CO}_2$ ) and incorporate it into their tissues. Animals eat plants and the carbon-14 then resides in their tissues.

Whilst the plants and animals live, the proportion of carbon-14 to carbon-12 remains constant (approximately,  $1:10^{12}$ ) but when they die the proportion of carbon-14 decreases as the carbon-14 decays to non-radioactive nitrogen. The age of carbon based relics can be estimated by measuring the amount of carbon-14 remaining in a sample of the relic.

It is known that the half-life of carbon-14 is 5730 years so, in simple terms, if it was discovered that a sample of an ancient wooden relic had *half* of the radioactivity of a living, or near dead, sample of wood it could be concluded that the wooden relic was over 5000 years old!

$$A = A_0 e^{-\lambda t}$$

eg,

where, A = radioactivity of dead wood  
in counts per second per gram ( $\text{counts s}^{-1} \text{ g}^{-1}$ ) of carbon  
 $A_0$  = radioactivity of live wood  
counts  $\text{s}^{-1} \text{ g}^{-1}$  of carbon  
 $\lambda$  = decay constant for  $^{14}\text{C}$  ( $3.84 \times 10^{-12} \text{ s}^{-1}$ )  
t = age of wooden relic

eg, A wooden relic has an activity of 9.50 counts per minute per gram of carbon. Live wood has an activity of 10.00 counts per minute per gram of carbon. What is the age of the wooden relic?

$$\begin{aligned}\ln(9.50/10.00) &= -\lambda t \\ \ln(10.00/9.50) &= \lambda t \\ t &= \ln(10.00/9.50) / \lambda = \ln(10.00/9.50) / 3.84 \times 10^{-12} \text{ s}^{-1} = 1.336 \times 10^{10} \text{ s} \\ t &\sim 424 \text{ yrs}\end{aligned}$$

Experimental procedures for establishing carbon-14 in carbon based material and estimating its age were originally developed by the American chemist Willard Libby in about 1946. He validated his procedures by determining the correct age of previously authenticated and known age Egyptian acacia wood artefacts.

With the advent of modern instruments, such as the **accelerator mass spectrometer (AMS, see footnote)** and our improved knowledge of the variations of atmospheric  $^{14}\text{CO}_2$  over the earth's surface at various periods in history, carbon dating techniques, for artefacts up to about 50 000 years of age, have achieved reasonable accuracy and reliability.

However, although modern methods of analysis can provide accurate carbon-14 measurements the translation of these into the age of the relic from which the analytical sample was derived can be much less certain. This is because there are a number of variables which are more difficult to quantify. Age estimates need to take into account fluctuations in atmospheric carbon-14 due to variations in cosmic ray activity and industrial pollution (ie, by the burning of fossil fuels and nuclear weapon testing). It is also important to consider the source of the relic and possible contamination from carbonates from ground water and organic acids from other organic matter in the vicinity of the relic. In order to address some of these issues a number of calibration charts have been produced which are used to correct the raw analytical data before estimating the age of the relic.

The AMS is designed to separate atomic particles of almost identical mass. It analyses very small samples of material (ie, milligram quantities, which is particularly useful in the case of carbon dating), and not only does it cleanly separate carbon-14 & carbon-12 it can also resolve nitrogen-14 and carbon-14. As a result, it can provide accurate carbon isotope ratios which can then be used to calculate the age of the analytical sample.

$$\text{eg, } ^{14}\text{C}/^{12}\text{C} = 1.2 \times 10^{-12} e^{-t/8270} \quad \text{where, } t \text{ is the age of the carbon based material}$$